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ELECTROCHEMICAL INVESTIGATION OF PALLADIUM COMPLEXES WITH ORGANIC SULPHIDES AND THEIR USE IN EXTRACTION DIFFERENTIAL PULSE POLAROGRAPHY

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Summary—Dialkyl-, amino-, keto- and ketoaminosulphide complexes of palladium(II) are shown to undergo one- or two-step reduction in a mixed acetonitrile–toluene solvent containing Bu_4NClO_4 at 0.1*M* concentration. The half-wave potentials of the complexes show a certain dependence on the ligand structure, a positive shift of the potentials being caused by an increase in the π-acceptor ability of the ligands. The limiting currents are proportional to the concentration of the complex, according to the Ilkovič equation. Fast-scan differential pulse polarography was applied to the determination of palladium(II) in the organic phase after extraction of its complex with dihexylsulphide.

There are a number of papers and reviews dealing with the co-ordination chemistry of ligands and chelates containing the thio-ether group in their structure.[1] These organic compounds are of some importance on account of their biological activity and also their usefulness as extraction reagents for the concentration and determination of metal ions.[2] The analytical application of organic extractants for the separation and determination of metals, in particular palladium, in the presence of the other platinum metals, is of special interest. This paper reports on the electrochemical reduction of palladium(II) complexes with organic sulphides, with composition PdL_mCl_2, where

$m = 1$, L = $C_{12}H_{25}SC_2H_4N$⬡ (I)

$C_6H_5COCH(CH_3)CH_2SC_2H_4N$⬡ (II)

$C_6H_5COCH(CH_2SC_6H_{13})_2$ (III)

$m = 2$, L = $C_6H_5COC_2H_4SC_8H_{17}$ (IV)

$(C_6H_{13})_2S$ (V)

$(C_8H_{17})_2S$ (VI)

in an acetonitrile–toluene mixture at the dropping mercury electrode, and discusses the possibility of determining palladium(II) by fast-scan differential pulse polarography (FSDPP) with dihexylsulphide (DHS) as an extractant. The general principles of extraction polarography used in the investigation have been described in a review.[3]

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EXPERIMENTAL

Apparatus

The electrochemical experiments were done with a PU-1 polarograph (USSR) for recording d.c. and a.c. polarograms, a dropping mercury electrode (d.m.e.) with $m = 1.96$ mg/sec at zero potential and controlled drop time $t = 0.21$ sec. Cyclic and FSDPP voltamperograms were obtained with a PA-3 polarograph and a stationary mercury drop electrode of type SMDE-1 (Czechoslovakia). All voltammetric measurements were made with a three-electrode cell at $25 \pm 0.1°$ with Ag/0.1*M* $AgNO_3$ in acetonitrile as a reference electrode, and a platinum wire as an auxiliary electrode.

Reagents

The organic sulphides and palladium complexes were prepared as described in the literature.[4–6] Their purity was checked by infrared spectroscopy and elemental analysis. Organic solvents were purified by the methods recommended in the literature[7] and were kept over 4A molecular sieves. Tetrabutylammonium perchlorate (0.1*M*) was used as background electrolyte. The solutions were deoxygenated by a stream of argon. The purity of the electrolyte was checked by recording blank polarograms with the d.m.e. The base-line for the solvent mixture was run as a check on electrochemical purity.

Solutions

Measurements were made on a 2:3 v/v mixture of the extracting and ionizing solvents: 0.15*M* Bu_4NClO_4 in acetonitrile as ionizing solvent and 0.05*M* DHS in toluene as the extractant. Stock solutions of organic sulphides were prepared by accurate direct weighing. The buffer solutions for the extraction were prepared from reagents of high purity.

Extraction procedure

A 5-ml portion of 0.05*M* DHS in toluene and a 25-ml portion of 10^{-5}–10^{-7}*M* aqueous solution of palladium(II) in 1*M* hydrochloric acid were shaken together in a separating funnel for 10 min. After separation of the phases by